29100 DUP

IGM88TC-108-752-G
CNRC 29100

# VISCOELASTIC BEHAVIOR OF POLYMER BLENDS

by

L.A. Utracki
National Research Council Canada
Industrial Materials Research Institute
75 De Mortagne, Boucherville, Que., Canada, J4B 6Y4

* Based on the text prepared for S.P.E. ANTEC-88 in Atlanta, GA.

# VISCOELASTIC BEHAVIOR OF POLYMER BLENDS

L.A. Utracki

National Research Council Canada

Industrial Materials Research Institute

75 De Mortagne, Boucherville, Que., Canada, J4B 6Y4

## ABSTRACT

There is a reciprocal relation between flow and structure in multiphase systems such as polymer blends or composites. For this reason characterization of these materials must be carried out under conditions which guarantees minimum modification of structure. The capillary rheometry is particularly ill suited as a test tool, but the small strain dynamic oscillatory method may provide the true material responses. Most frequently these are expressed as frequency, $\omega$, dependent storage and loss shear moduli, G' and G", or real and imaginary viscosities, $\eta' = G''/\omega$ and $\eta'' = G'/\omega$. However, two other methods of data presentation seem to be more sensitive to melt structure. They are the Cole-Cole plot of $\eta''$ vs. $\eta'$ and the relaxation spectrum. Frequently, both of them indicate a binomial response. Various mechanisms leading to such behavior will be discussed.

## INTRODUCTION

Recently, rheology as a tool for analysis of polymer alloys and blends, PAB, was discussed [1-3]. In the first two references general principles determining the flow properties of PAB were presented. Reference [3] dealt with miscible and immiscible polyethylene blends.

In the absence of a better method of classification of polymer blend flow behavior the log-additivity rule may be used:

$$\log F = \sum w_i \log F_i \qquad (1)$$

where F is a melt rheological function, e.g. shear or extensional viscosity, $\eta$ or $\eta_E$, shear storage or loss moduli, G' or G" and $w_i$ is a measure of composition, usually expressed as weight or volume fraction of component i. The use of Eq (1) makes it possible to distinguish Positive Deviating Blends (PDB), Negative DB (NDB) and PNDB with a sigmoidal dependence. These three classes occur (for different reasons) in both miscible and immiscible blends [4]. Contrary to frequent believe the concentration dependence of a rheological function does not indicate blend miscibility or immiscibility.

The other rheological methods of analysis used for information on PAB miscibility are: (i) lack of agreement between the steady state and dynamic responses, e.g. plot of shear stress components, $\sigma_{11} - \sigma_{22}$ vs. $\sigma_{12}$, being different from 2G' vs. G" dependence [5,6]; (ii) Cole-Cole plot of the imaginary vs. real part of dynamic viscosity, $\eta$" vs. $\eta$' [7]; (iii) initial

slope of the stress growth function in uniaxal extension, $\eta_E^+$ [8]; (iv) the relaxation spectrum [9], and others. The approach (i) involves two sets of measurement in the rotational rheometer. The difference can originate in the strain effect on morphology within these usually low deformation rates. Method (ii) uses a deviation from the semi-circular Cole-Cole dependence. Method (iii) requires precise determination of $\eta_E^+$ at short times and usually empirical correlation between the slope, $S_i \equiv \partial \ln \eta^+ / \partial \ln t$, and sample polydispersity. Method (iv) is the most general.

## THEORY

The frequency relaxation spectrum can be computed from any dynamic function of frequency. In particular [10]:

$$H_G(\omega) = (\pm 1/\pi\omega)\, Im\, G^*(\omega e^{\pm i\pi}) \tag{2}$$

$$H_G(\omega) = (\pm 2/\pi\omega)\, Im\, G'(\omega e^{\pm i\pi/2}) \tag{3}$$

$$H_G(\omega) = (2/\pi\omega)\, Re\, G''(\omega e^{\pm i\pi/2}) \tag{4}$$

where $H_G$ is Gross relaxation spectrum of frequency ($\omega$), and *Im* and *Re* respectively, indicate the imaginary and real part of the complex function G*.

As long as the frequency dependence of dynamic viscosity, $\eta' = G''/\omega$, can be described by the relation [8]:

$$\eta' = \eta_0 [1 + (\omega\tau)^{m_1}]^{-m_2} \tag{5}$$

(where: $\eta_0$ is the zero-shear viscosity, $\tau$ - relaxation time, $m_1$ and $m_2$ parameters related to polydispersity) from Eq (4) the frequency relaxation spectrum can be expressed as:

$$H_G(\omega) = (2\eta_0/\pi) r_1^{-m_2} \sin m_2\theta_1 \tag{6}$$

where $$r_1 \equiv \left[1 + 2(\omega\tau)^{m_1}\cos(\pi m_1/2) + (\omega\tau)^{2m_1}\right]^{\frac{1}{2}}$$

$$\theta_1 \equiv \arcsin\left\{(\omega\tau)^{m_1} r_1^{-1}\sin(\pi m_1/2)\right\}$$

The Cole-Cole relation for complex viscosity, $\eta^*$, was generalized by Havriliak and Nagami [11]. The dependence proposed by these authors is given by:

$$G^*/\omega \equiv \eta^* = \eta_0 \left[1 + (i\omega\tau_2)^{1-\alpha}\right]^{-\beta} \tag{7}$$

For simple liquids setting $\alpha = 0$ and $\beta = 1$ the original Cole-Cole relation is recovered. From Eqs (2) and (7):

$$H_G = (\eta_0/\pi) r_2^{-\beta} \sin\beta\theta_2 \tag{8}$$

with:

$$r_2 \equiv \left\{\left[1 - (\omega\tau_2)^{1-\alpha}\sin(\pi\alpha/2)\right]^2 + (\omega\tau_2)^{2(1-\alpha)}\cos^2(\pi\alpha/2)\right\}^{\frac{1}{2}}$$

$$\theta_2 \equiv \arctan\left\{\left[(\omega\tau_2)^{1-\alpha}\cos(\pi\alpha/2)\right]/\left[1 - (\omega\tau_2)^{1-\alpha}\sin(\pi\alpha/2)\right]\right\}$$

and:

$$G''/\omega \equiv \eta' = (\eta_0/r_2^{\beta})\cos\beta\theta_2 \tag{9}$$

$$G'/\omega \equiv \eta'' = (\eta_0/r_2^{\beta})\sin\beta\theta_2 \tag{10}$$

For simple liquids $\eta'' = \eta'(\omega\tau_2=1)$, i.e. for $\omega = 1/\tau_2$ the dependencies: $\eta' = \eta''$ or $G' = G''$ are obtained.

It is worth noting that not only does the frequency relaxation spectrum contain the same information as $\eta'$ or $\eta''$ but also that (for systems obeying Eq (7)) from Eqs (8) and (10):

$$\eta'' = \pi H_G(\omega) \tag{11}$$

i.e. the Cole-Cole plot provides direct information on the modality of relaxations as much as the relaxation spectrum does. However, while the $\eta''$ vs $\eta'$ plot is a pictorial illustration of the relaxations, $H_G$ in addition provides a means for generating a diversity of linear viscoelastic functions from the exact mathematical dependencies [12].

## EXPERIMENTAL

Four immiscible and one miscible blends were examined. The characteristics of the homopolymers are listed in Table 1. The blends (see Table 2) were prepared using a ZSK-30 twin screw extruder. After granulation and drying the pellets were used to mold 2mm thick specimens for the Rheometrics Mechanical Spectrometer, RMS-605. All tests were done within the linear viscoelastic

range of strains under a blanket of dry $N_2$ at frequencies $\omega = 10^{-2}$ to $10^2$ (rads/s).

## RESULTS AND DISCUSSION

It was not surprising that in miscible System I both Eqs (5) and (7) provided an excellent fit with the standard deviation $\sigma = \pm 0.3\%$ [8, 14]. Unexpected, however, was the almost equally good fit to data of immiscible Systems II, III and V ($\sigma \lesssim 0.6\%$, dependent on composition). For all systems the relaxation spectra were computed from Eq (3) and then other linear viscoelastic functions were calculated in good agreement with the directly measured results. The coordinates of the maximum on the reduced relaxation spectrum:

$$\bar{H}_G(\omega) \equiv H_G(\omega)/\eta_0 \tag{12}$$

provided a good indication of blend miscibility [8, 13].

In polyolefin blends II and III the yield stress in storage, $G'_y$, and loss, $G''_y$, moduli played a minor role and the raw experimental data followed Eqs (5) or (7) quite well. On the other hand in systems IV and V strong apparent yield stress was observed [13, 15]. Interestingly enough $G'_y > G''_y$ and the values tended to decrease on addition of compatibilizer. Apparently responsible for yield phenomena the three-dimensional network was created by interacting droplets of the dispersed phase; larger the droplets and higher their concentration, larger the apparent yield stress. This mechanism of yielding was further supported by observed behavior of the apparent yield stress,

$\sigma_y = G'_y$ or $G''_y$; at frequencies above certain critical value $\sigma_y(\omega > \omega_c)$ = const., but below it $\sigma_y$ decreased with lowering of $\omega$ to zero. In the latter case apparently the time scale of the test was long enough allowing the droplets to flow by each other and dissipate the energy which at higher frequency test would have to be stored by the deformed network. The frequency dependent structural change or an apparent yield stress can be expressed as:

$$\sigma_y(\omega) = \sigma_y[1 - \exp\{-\tau_y\omega\}] \tag{13}$$

where $\sigma_y$ and $\tau_y$ are parameters, the first related to the high frequency instantaneous yield stress, the second to a characteristic relaxation time of a tri-dimensional structure in which the apparent yield originates (see Fig. 1). The $\tau_y$ is usually much longer than the $\tau$'s in relaxation spectrum, Eq (6) or Eq (8). As a result, the yield effects also appear as bimodalities on the Cole-Cole plot and in relaxation spectrum.

For practical reasons subtracting $\sigma_y$ from the dynamic function prior to computation of $H_G$ was found to be simpler than fitting the data to algebraically complicated expression generated by combining Eqs (5) or (7) with (13). The rheological evaluation of blends IV and V involved subtracting the apparent yield stress from experimental data, e.g.:

$$G'' = G''_a - G''_y \tag{14}$$

then fitting $G'' = G''(\omega)$ data to either Eq (5) or Eq (7) and computing $H_G$

from Eq (6) or Eq (8), respectively. Consequently, the other viscoelastic functions, e.g. G' or G(t), did not contain the apparent yield stress effects and were compared with the experimental data from which $\sigma_y$ was substracted, similarly as $G''_a$ in Eq (14). Good agreements between the computed and measured values were obtained.

Use of the Cole-Cole plot was found to be simpler but less informative and flexible. The problems already started with homopolymers such as polyethylenes, resins No. 4 to 7 in Table 1. The bimodality of the distribution of molecular weight [14] resulted in a complex $\eta''$ vs. $\eta'$ dependence (see Fig. 2) indicating bimodality of relaxation times which mitakenly could be taken for a sign of phase separation.

It is worth recalling that: (1) bimodality in Cole-Cole plot has been observed for homologous blends of sharp polystyrene fractions [7, 16]; (2) bimodality in Cole-Cole plot for immiscible polystyrene/polycarbonate blend as well as for the compatibilized blend of these two polymers with tetramethylene-polycarbonate has been reported [17, 18]. The Cole-Cole graph provides information on relaxations occurring within the blend, irrespective of whether these take place in two phases of coarse blends or in true solutions.

If rheology is affected by two-phase dispersion the investigations must concentrate on effects of the interphase. It is worth pointing out that the specific interfacial area is discontinuous function of the concentration. The concentration at which the discontinuity is observed is related to sudden changes of blend morphology, e.g. phase inversion. Consequently, it is from

the plot of a rheological function vs. composition that the information on blend miscibility in the molten state can originate. One may be tempted to relate the breadth of relaxation spectrum or that of the Cole-Cole plot to immiscibility. This however is equivalent to discussing $\eta_0$ vs $w_i$ dependence which, as mentioned in the Introduction, does not provide a unique answer. The searched for rheological function must be more sensitive to the interphase than breadth of the relaxation spectrum, i.e. $\eta_0$. However, since all the information on dynamic flow behavior is incorporated in relaxation spectrum the function sensitive to the interface must be there also.

It should be noted that there is extensive information in the literature on the effect of blending of homologous polymers on relaxation spectrum (e.g. see [19] and the cited references). Assumption of miscibility leads to calculation of molecular weight averages as functions of the blend composition, $w_i$, and these in turn make it possible to theoretically predict variation of $H_G$ with $w_i$. Comparing the experimental curves with those computed from assumed miscibility provides a direct test for assessing the system miscibility.

One simplification is worth mentioning. For systems with a monomodal relaxation spectrum expressed in the reduced form, Eq (12), the integral:

$$\int_0^\infty H_G d\omega = 1 \qquad (15)$$

i.e. the relaxation spectrum is characterized by the coordinates of the

maximum ($H_{G,max}$, $\omega_{max}$). It can be theoretically shown that $H_{G,max}$ depends mainly on polydispersity and $\omega_{max}$ on molecular weight. Calibrating these functions and comparing them with the experimental results makes it possible to determine blend miscibility from the dynamic test results.

It has been recognized that the rheological behavior depends on liquid density or on the free volume. Measurements of blend density, $\rho$, vs. composition provide a direct evidence on interactions in miscible and immiscible systems. In the latter case the interactions are limited to the interphase. Since the effects of pressure and temperature on simple liquid density are easy to account for [20] the interactive part can be subtracted and compared with the rheological responses. Sensitivity of this approach varies from one system to the next [8]. The knowledge of $\rho$ vs. $w_i$ is important in analysis of the flow behavior of polymer blends with unknown miscibility.

## REFERENCES


1. L.A. Utracki, S.P.E. Techn. Papers, 32, 286 (1986).
2. L.A. Utracki, J. Elastom. Plast., 18, 177 (1986).
3. L.A. Utracki and B. Schlund, S.P.E. Techn. Papers, 33, 1002, (1987).
4. L.A. Utracki, Ch. 5.1 in "Current Topics in Polymer Science", R.M. Ottenbrite, L.A. Utracki and S. Inoue, Eds., Hanser Publ., München (1987).
5. H.-K. Chuang and C.D. Han, J. Appl. Polym. Sci., 29, 2205 (1984).
6. L.A. Utracki, M.M. Dumoulin and P. Toma, Polym. Eng. Sci., 26, 34 (1986).
7. J.P. Montfort, G. Marin, J. Arman and Ph. Monge, Polymer, 19, 277 (1978).
8. L.A. Utracki and B. Schlund, Polym. Eng. Sci., 27, 1512 (1987).
9. L.A. Utracki, 37th Canadian Chem. Eng. Conf., Montreal, Que., 18-22 May (1987).
10. B. Gross, "Mathematical Structure of the Theories of Viscoelasticity", Hermann, Paris (1953).
11. S. Havriliak and S. Nagami, Polymer, 8, 161 (1967).
12. J.D. Ferry, "Viscoelastic Properties of Polymers", third ed., J. Wiley and Sons, New York (1980).
13. L.A. Utracki and P. Sammut, Report to IUPAC W.P. 4.2.1 (1986); Polym. Eng. Sci., 28, 0000 (1988).
14. B. Schlund and L.A. Utracki, Polym. Eng. Sci., 27, 259 (1987).
15. L.A. Utracki, A. M. Catani, G.L. Bata, M.R. Kamal and V. Tan, J. Appl. Polym. Sci., 27, 1913 (1982).
16. J.P. Montfort, Doctorat d'Etat, Université de Pau (1984).
17. C. Wisniewsky, G. Marin and Ph. Monge, Eur. Polym. J., 21, 479 (1985).
18. C. Belaribi, G. Marin and Ph. Monge, Eur. Polym. J., 22,481, 487 (1986).
19. H. Watanabe and T. Kotaka, Macromolecules, 20, 530, 535 (1987).
20. L.A. Utracki, J. Rheol., 30, 829 (1986).

**TABLE 1. CHARACTERISTICS OF HOMOPOLYMERS**

| No | Polymer | Manufacture | Code | $T_m$ (°C) | $\overline{M}_w.10^{-3}$ | $\overline{M}_w/\overline{M}_n$ |
|---|---|---|---|---|---|---|
| 1. | Polyethyleneterephthalate | Kodak | PET | 257 | 55 | 2.2 |
| 2. | Polyamide-6,6 | Dupont | PA-66 | 258 | 36 | 2.4 |
| 3. | Linear low density polyethylene | Exxon | LPX-30 | 126 | 133 | 3.4 |
| 4. | Linear low density polyethylene | Exxon | LLDPE-10 | 129 | 152 | 10.6 |
| 5. | Linear low density polyethylene | Exxon | LPX-24 | 128 | | |
| 6. | Low density polyethylene | Exxon | LDPE-1 | 114 | 64.2 | 4.1 |
| 7. | Low density polyethylene | BP Chem. | LDPE-2 | 122 | 306 | 17 |
| 8. | Isotactic polypropylene | Hercules | PP | 165 | | |
| 9. | Polystyrene | BP Chem. | PS | - | 268 | 2.0 |

**TABLE 2. IDENTIFICATION OF BLENDS**

| System No. | Polymer in Table 1 | Type |
|---|---|---|
| I | 3 and 4 | Miscible |
| II | 3 and 6 | Immiscible |
| III | 5 and 8 | Immiscible |
| IV | 1 and 2 | Immiscible |
| V | 7 and 9 | Immiscible |

## LEGEND FOR FIGURES

Fig. 1. Frequency dependent dynamic viscosity for System IV (30% PA-66) at 280 and 300°C. The curves were generated using Eqs (2) and (10). Data [17].

Fig. 2. Cole-Cole plot for miscible (System I) and immiscible (System II) polyethylene blends. Data [8].

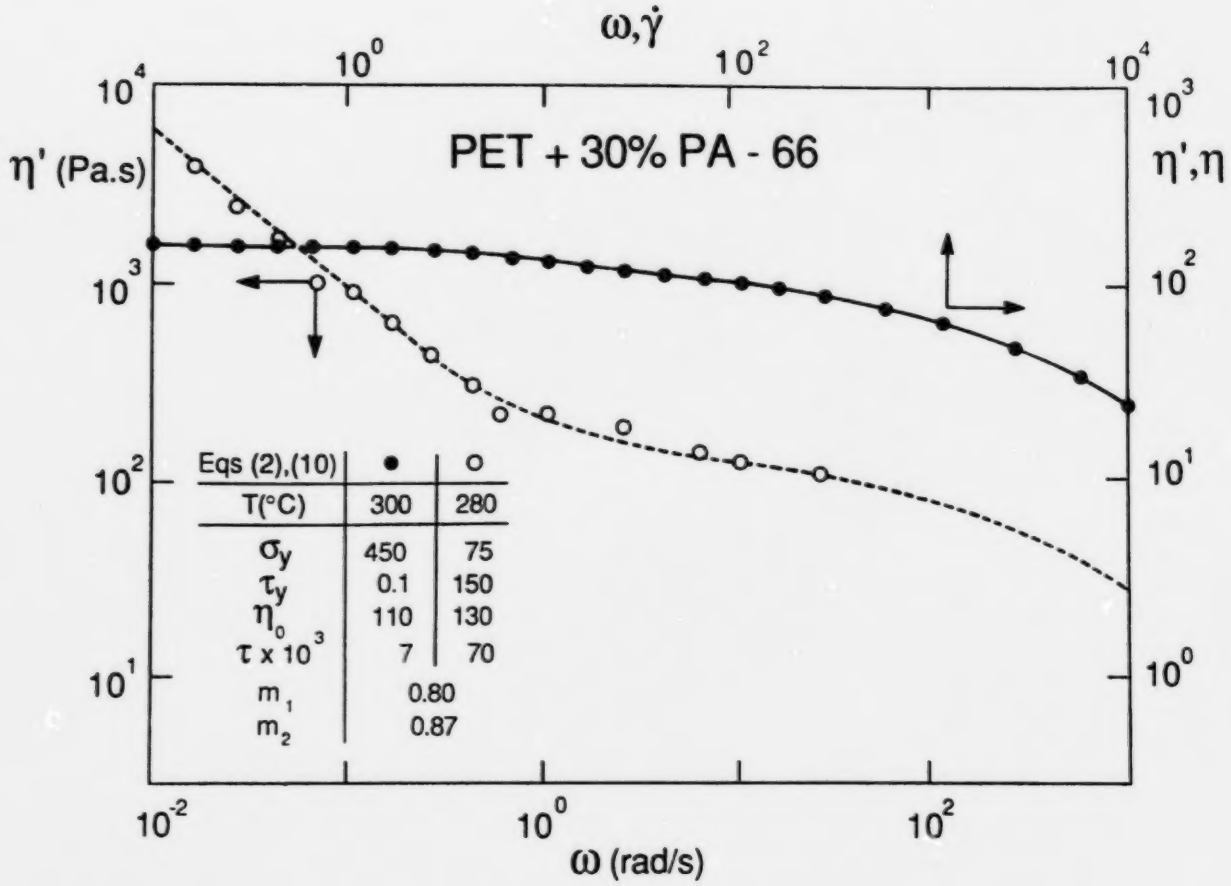


Fig. 1. Frequency dependent dynamic viscosity for System IV (30% PA-66) at 280 and 300°C. The curves were generated using Eqs (2) and (10). Data [17].

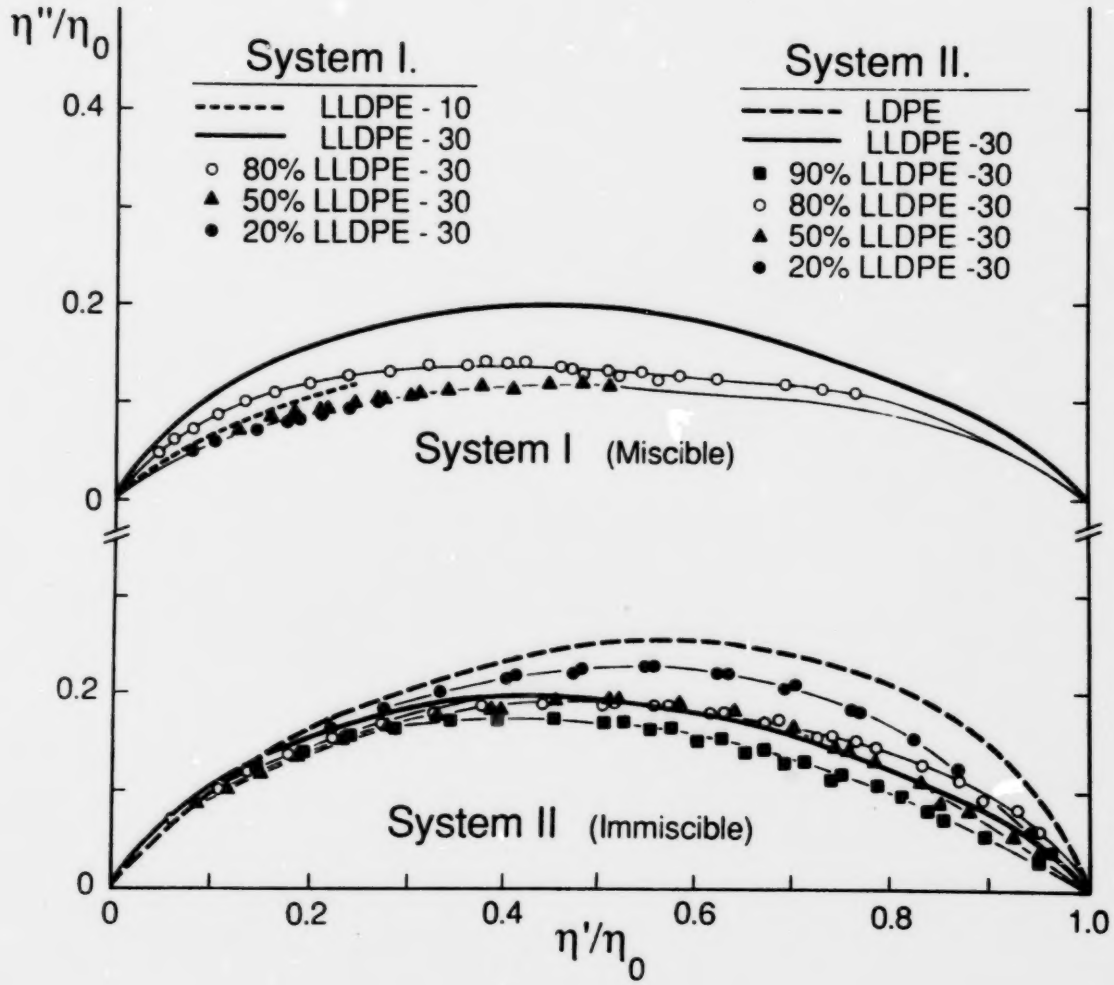


Fig. 2. Cole-Cole plot for miscible (System I) and immiscible (System II) polyethylene blends. Data [8].